Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

01: Introduction

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Environmental Monitoring & Data Quality Workshop
29 March 2011

US Army Corps of Engineers
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Class Behavior

- Questions encouraged
- For extended discussions or project-specific needs, please go to instructors during break or after class
- Focus on completing the overall agenda
- We want all the students to have the benefit of the course – lots of material to cover!

Class Topics

- Introduction
- Conceptual Site Model Inputs: Range Types, Layouts, and Munitions
- Use of Geophysics and Other Remote Sensors to Guide MC Sampling
- Introduction to MC
- Primary and Secondary Explosives
- Propellants
- Metals
- Chemical Warfare Materiel
- MC Considerations Related to MEC Operations
- MIDAS Demo

Report Documentation Page

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Introductions

- Instructor Introductions

Class Demographics

- ► Employers?
  - DoD
  - Prime Contractors
  - Labs
- ► Professional Background?
  - Chemists
  - Other Scientists
  - Engineers
  - Other
- ► MMRP Experience?
  - >5 years
  - 1-5 years
  - <1 year
- ► Why are you here?
  - Work in the field
  - Hope to do work
  - Academic interest

Why MC?

- MMRP combines Munitions and Explosives of Concern (MEC, formerly known as Ordnance and Explosives, OE) and MC (formerly known as HTRW related to OE) into a single program element for funding/reporting
- From DOD Management Guidance for DERP, September 2001
  - ► The ***Military Munitions Response program*** category is defined as response actions (i.e., the identification, investigation, and removal actions, remedial actions, or a combination of removal and remedial actions) to address military munitions (i.e., UXO or WMM*) or ***the chemical residues of munitions***.

*Terminology has since changed to DMM.

Why MC?

- National Defense Authorization Act (NDAA) FY 2002, directed DOD to:
  - ► Develop and maintain an inventory of all defense sites* known or suspected to contain UXO, DMM, and MC
  - ► Develop a protocol to prioritize inventoried sites
  - ► Establish a new program element within the environmental restoration account to track remediation of UXO, DMM, and MC
- OSD direction and USACE ER 200-3-1 requirements to go to Remedial Process for MMRP (and to work IAW rather than consistent with CERCLA/NCP)
- Remedial Process rather than Removal Process focuses on the contamination rather than treating all contamination as an imminent hazard, so MC and MEC are addressed during the same action rather than consecutively

MMRP Terminology

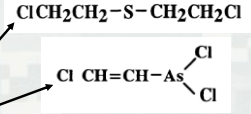
- Munitions Constituents (MC)
- Military Munitions
- Munitions and Explosives of Concern (MEC)
- Unexploded Ordnance (UXO)
- Discarded Military Munitions (DMM)
- MC as Explosive Hazard
- Defense Site
- Munitions Response Area (MRA)
- Munitions Response Site (MRS)

MC Definition

"Any materials originating from unexploded ordnance, discarded military munitions, or other military munitions, including explosive and nonexplosive materials, and emission, degradation, or breakdown elements of such ordnance or munitions."
(10 U.S.C. 2710 (e) (3))*
(originally referenced as (4))

MC Examples

- Explosives and Breakdown Products
  - 2,4,6-Trinitrotoluene (TNT)
  - Cyclotrimethylenetrinitramine (RDX)
  - Cyclotetramethylenetetranitramine (HMX)
- Pyrotechnics/Propellants
  - Perchlorate
- Smokes
  - White Phosphorus (WP)
- Chemical Warfare Materiel, Industrial Chemicals, and Breakdown Products
- Metals



Military Munitions

- "All ammunition products and components produced or used by or for the U.S. DOD or the U.S. Armed Services for national defense and security, including military munitions under the control of the DOD, the US Coast Guard, the US DOE, and National Guard personnel. The term military munitions includes: confined gaseous, liquid, and solid propellants, explosives, pyrotechnics, chemical and riot control agents, smokes, and incendiaries used by DOD components, including bulk explosives and chemical warfare agents, chemical munitions, rockets, guided and ballistic missiles, bombs, warheads, mortar rounds, artillery ammunition, small arms ammunition, grenades, mines, torpedoes, depth charges, cluster munitions and dispensers, demolition charges, and devices and components thereof. Military munitions do not include wholly inert items, improvised explosive devices, and nuclear weapons, nuclear devices, and nuclear components there-of. However, the term does include non-nuclear components of nuclear devices, managed under DOE's nuclear weapons program after all required sanitization operations under the Atomic Energy Act of 1954, as amended, have been completed.
(40 CFR 260.10)

Not just energetics and metals

Munitions and Explosives of Concern (MEC) Definition

- This term, which distinguishes specific categories of military munitions that may pose unique explosives safety risks means:
  - ►Unexploded Ordnance (UXO),
  - ►Discarded Military Munitions, or
  - ►Munitions Constituents present in high enough concentrations to pose an explosive hazard

Unexploded Ordnance (UXO) Definition

- Military munitions that have been:
  - ►Primed, fuzed, armed, or otherwise prepared for action, and have been
  - ►Fired, dropped, launched, projected or placed in such a manner as to constitute a hazard to operations, installation, personnel, or material and
  - ►Remain unexploded either by malfunction, design, or any other cause.

(40 CFR 266.201)

Discarded Military Munitions (DMM) Definition

- "Military munitions that have been abandoned without proper disposal or removed from storage in a military magazine or other storage area for the purpose of disposal. The term does not include unexploded ordnance, military munitions that are being held for future use or planned disposal, or military munitions that have been properly disposed of, consistent with applicable environmental laws and regulations."

(10 U.S.C. 2710 (e) (3))

MC as Explosive Hazard ("Explosive Soil")

- The following are to be treated as explosive hazards (HD 1.1):
  - Primary (Initiating) Explosives – Soil containing >2% by weight of any primary explosive or mixture of primary explosives
  - Secondary explosives or propellants (Nitrocellulose, Nitroglycerine, Nitroguanadine) – Soil containing >10% by weight of either any of these or a mixture of them

DOD 6055.09-M, V7.E4.4.1

Defense Site Definition

- "… applies to locations that are or were owned by, leased to, or otherwise possessed or used by the Department of Defense. The term does not include any operational range, operating storage or manufacturing facility, or facility that is used for or was permitted for the treatment or disposal of military munitions."

Ranges on Formerly Used Defense Sites are examples of Defense sites

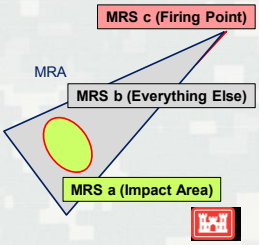
(10 U.S.C. 2710 (e) (1))

Munitions Response Area/Site (MRA/MRS)

$$MRA\,(acres) = \sum (MRSa + MRSb + MRSc \ldots)\,acres$$

- MRA
  - Any area on a defense site that is known or suspected to contain UXO, DMM, or MC (e.g., former ranges or munitions burial areas)
  - Must be comprised of at least one MRS, but may contain multiple MRSs
- MRS
  - Defined as "a discrete location within an MRA that is known to require a munitions response"

(32 CFR Part 179.3)



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FUDS Funding Profile

All service profiles have points where the IRP and MMRP categories switch places in funding totals. Active installation MMRP funding profiles are increasing faster than FUDS due to assigned MMRP metrics.

- For current FY and FY12, MMRP category is funded substantially lower than IRP category.
- Both categories are scheduled to become equally funded in FY13.
- The MMRP category is scheduled to get a dramatic upsweep in funding in FY19 in conjunction with the IRP goal of FY20.

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Questions?

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Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

10: MIDAS Demo

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MIDAS

Munition Items Disposition Action System

https://midas.dac.army.mil

MIDAS

- Need to register
- Need User Name and password
- Will be CAC enabled by the end of the year

Can Search by

- NSN (National Stock Number)
- DODIC (DoD Identification Code)
- Family
- Nomenclature
- Drawing Number

Munitions reports available

- Detail Report
- Less Bulk Report
- Less Compounds Report
- MCP (Munitions, Components, Parts) Report
- Primary Component Part Report
- TDP (Technical Data Package) Report
- TRI (Toxic Release Inventory) Report
- Summary of all Compounds Report
- Firing Point / Impact Point Report
- PEP Structure Report
- PEP Summary Report

Practice Searches

- Cartridge, Caliber .30, AP, M2
- Cartridge, Caliber .50, AP, M2
- Cartridge, 105-mm, HE, M1
- Projectile, 155-mm, HE, M102, MK I, MK IA1

Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

02: Conceptual Site Model Inputs:
Range Types, Layouts, and Munitions

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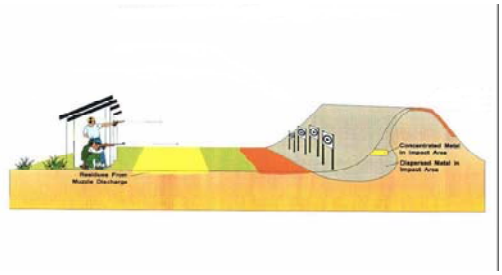
Range Types

FUDS Range Types

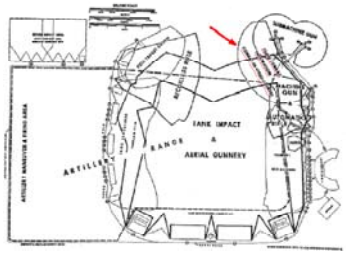
- Small Arms
- Multiple Weapons Type
- Field Artillery
- Mortar
- Shoulder-Launched Small Rocket
- Medium Caliber Rocket
- Heavy Rocket and Guided Missile
- Recoilless Rifle
- Davy Crockett
- Tank
- Anti-Tank Gun
- Antitank Guided Missile
- Anti-Aircraft Artillery
- Hand and Rifle Grenade
- 40mm Grenade Launcher
- Flame Thrower
- Mine, Boobytrap, and Demolition Area
- Chemical Warfare Training Area
- Helicopter Weapons
- Fixed Wing Air-to-Air Weapons
- Fixed Wing Air-to-Ground
- Maneuver
- Coast Artillery
- Open Burn/Open Detonation (OB/OD)

Range Layouts

Small Arms

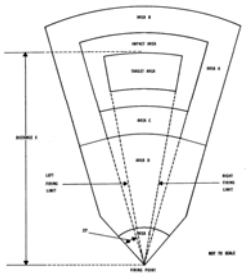


Multiple Weapons Type

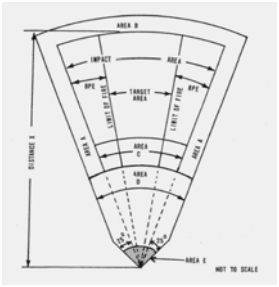


Typical Division Range Layout, Circa 1964

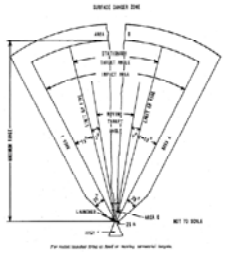
Artillery



Mortars

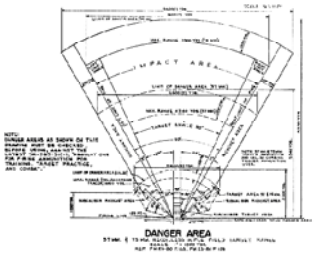


Shoulder-Launched Small Rocket



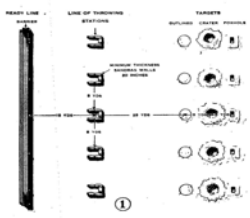
3.5 inch and 66-mm Shoulder-Launched Rocket Range, Circa 1968

Recoilless Rifle

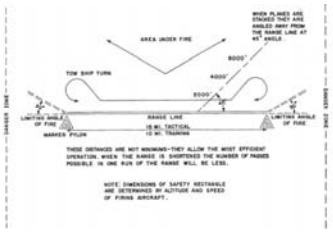


Recoilless Rifle Field Target Range, Circa 1951

Grenades

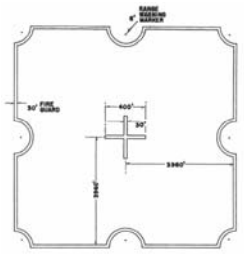


Fixed Wing Air-to-Air Weapons



Fixed Aerial Gunnery Range, Circa 1945

Fixed Wing Air-to-Ground



Tactical Bombing Range, Circa 1945

Types of Munitions

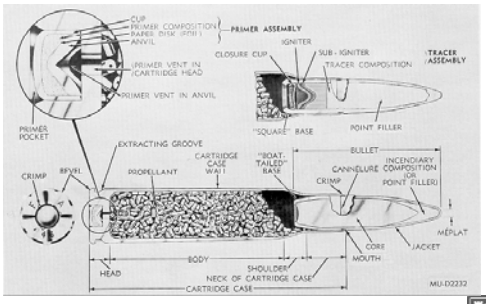
Types of munitions

- Small Arms
- Mortars
- Medium Caliber Ammunition
- Artillery
- Rockets
- Grenades
- Mines
- Bombs
- Pyrotechnics

Small Arms

- .50 caliber or smaller and shotgun ammunition
- Weapons: Pistols, Rifles, Machine Guns, Shotguns
- Found on:
  - Small Arms Range
  - Multiple Weapons Type Range
  - Tank Range
  - Helicopter Weapons Range
  - Fixed Wing Air-to-Air Weapons Range
  - Fixed Wing Air-to-Ground Range
  - Maneuver Range

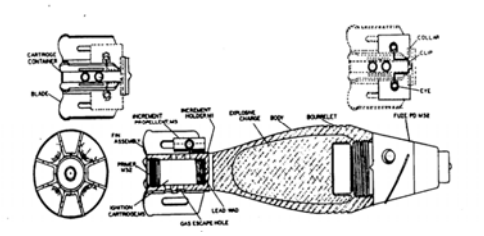
Small Arms Ammunition



Mortars

- Mortar Shells: 60-mm, 81-mm, 3-inch Trench, 4-inch, 4.2-inch, 6-inch Trench
- Found on: Mortar Ranges

Mortar Ammunition

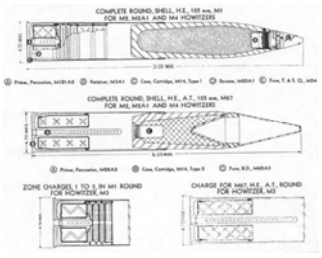


60-mm HE Mortar Round, Circa 1960

Artillery (Large Caliber Ammunition)

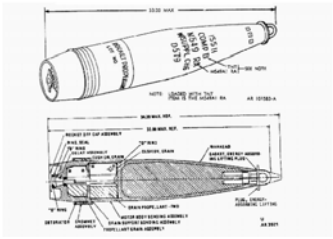
- 37-mm and larger shells
- Found on:
  - ►Field Artillery Range
  - ►Tank Range
  - ►Anti-Tank Gun
  - ►Coast Artillery Range

Artillery Ammunition



Shell, Semi-Fixed

Artillery Ammunition (2)

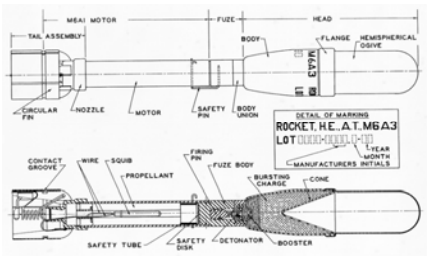


Projectile, 155-mm, HERA, M549 and M549A1

Rockets

- Found on:
  - Shoulder-Launched Small Rocket Ranges
  - Medium Caliber Rocket Ranges
  - Heavy Rocket and Guided Missile Ranges
  - Recoilless Rifle Ranges
  - Davy Crockett Common Range
  - Antitank Guided Missile Ranges
  - Helicopter Weapons Ranges
  - Fixed Wing Air-to-Air Weapons Ranges
  - Fixed Wing Air-to-Ground Ranges

Shoulder-Launched Small Rocket

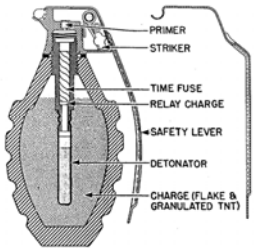


Rocket, 2.36-Inch Antitank, M6A3

Grenades

- Found on:
  - ►Multiple Weapons Type Ranges
  - ►Hand and Rifle Grenade Range
  - ►40mm Grenade Launcher Range

Hand Grenades

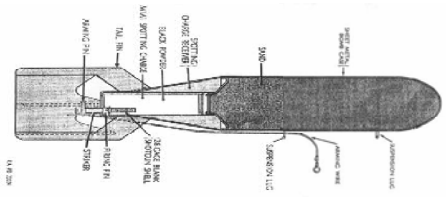


Grenade, Hand, Fragmentation, MK II, MK IIA1

Bombs

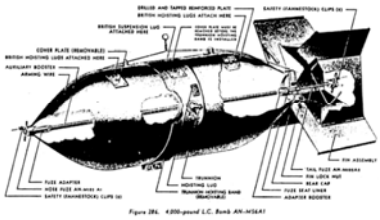
- Found on:
  - ►Fixed Wing Air-to-Ground Ranges

Practice Bomb



Bomb, Practice, 100 Pound, M38A2

Bomb

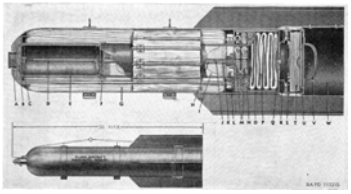


Bomb, Light Case, 4,000 LB AN-M56 & AN-M56A1

Pyrotechnics

- Found on many range types

Flares



Flare, Aircraft, Parachute, M26 & AN-M26

Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

04: Introduction to Types of MC

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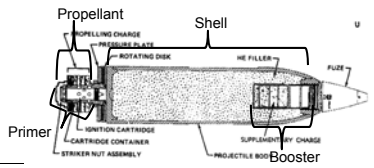
Topics

- Where in the Munitions does MC come from?
- What are the MC we'll talk about?
- What are Typical Methodologies for MC?
- Where can we find out what MC is in a particular munition?

Sources of MC in Munitions

- Main Components
  - ► Shell
  - ► Filler
  - ► Case
  - ► Propellant
- Minor Components
  - ► Primer
  - ► Fuze
  - ► Booster



Examples of MC

- Filler
  - Secondary explosives (TNT, RDX) (also Booster)
  - Chemical agents (Mustard, Lewisite, Tabun, Soman, VX)
  - Riot control (Tear gas: CN, CS, Vomiting agents)
  - Pyrotechnics
    - Incendiaries (metals)
    - Tracers (perchlorate, metals)
    - Smokes and Obscurants (Hexachloroethane (HC), White Phosphorus (WP), metals)
  - Miscellaneous Other Fills (Incapacitating agents, Simulants)

Examples of MC (Cont'd)

- Armor Piercing/Penetrators
  - Tungsten
  - Depleted Uranium (DU)
- Propellants
  - Black powder
  - Nitrocellulose (NC), nitroglycerine (NG), and nitroguanidine (NQ)
  - Perchlorate

Examples of MC (Cont'd)

- Case
  - Metals
- Primers, Fuzes
  - Primary Explosives

Typical Methodology More Acronyms!

- High Performance Liquid Chromatography (HPLC, also referred to as LC)
  - ► Coupled with Ultraviolet Spectrometry (UV) = LC/UV
  - ► Coupled with Mass Spectrometry (MS) = LC/MS
- Gas chromatography (GC)
  - ► Coupled with Mass Spectrometry (MS) = GC/MS
  - ► Coupled with Electron Capture Detector (ECD) = GC/ECD
  - ► Coupled with Nitrogen-Phosphorus Detector (NPD) = GC/NPD

Typical Methodology More Acronyms! (Cont'd)

- Inductively-Coupled Plasma (ICP)
  - ► Coupled with Atomic Emission Spectrometry (referred to as ICP)
  - ► Coupled with Mass Spectrometry (MS) = ICP-MS
- X-Ray Fluorescence Spectrometry (XRF)
- Graphite Furnace Atomic Absorption Spectrophotometry (GFAA)
- Cold Vapor Atomic Absorption Spectrophotometry (CVAA)

Typical Methodology More Acronyms! (Cont'd)

- Ion Chromatography (IC)
  - ► Coupled with Mass Spectrometry (MS) = IC-MS
- Immunoassay
- Colorimetry (Visible Spectrophotometry)

Sources of MC Information

- Technical Manuals
  - ► Advantages:
    - Period of use information available (all 60mm mortars are not equal)
    - Specific data available for specific munitions
    - Successful use encourages team interaction between Safety Specialists and Chemists
  - ► Disadvantages
    - Limited availability of appropriate TMs
    - Not all safety specialists understand how to help look for MC data (not their focus!)
    - Understanding of munitions nomenclature is key to understanding TMs; steep learning curve for the non-munitions expert
    - Even if you have electronic files, word searches only work if you know the right word to search on!

Sources of MC Information

- MIDAS

LIVE DEMO LATER!!

  - ► Advantages
    - Database with advanced search capabilities and reporting; even those with less knowledge of nomenclature can probably stumble on the answer faster with a database than with TMs
    - Available to DoD employees and DoD contractors (with sponsor)
  - ► Disadvantages
    - Understanding of munitions nomenclature is key to understanding; steep learning curve for the non-munitions expert
    - Period of use data not available
    - Obsolete munitions may not be available

Questions?

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Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

05: Primary and Secondary Explosives

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Environmental Monitoring & Data Quality Workshop
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Primary Explosives

What are Primary Explosives?

- Primary explosives are easily detonated by heat, spark, impact, or friction.
- Typically used in small quantities due to sensitivity

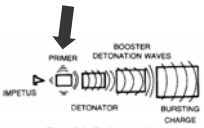


Figure 3-1. Explosive train.

Source: TM 9-1300-214 Military Explosives, Sep-1984

Examples of Primary Explosives

Primary Explosive	Typical Use
Lead Azide*	Initiator for high explosives
Mercury Fulminate*	Initiator for high explosives
Diazodinitrophenol (DDNP)	Priming compositions, commercial blasting caps.
Lead Styphnate*	Priming compositions, ignition of lead azide
Tetracene	Priming compositions, boosters
Potassium Dinitrobenzofuroxane (KDNBF)	Priming compositions
Lead Mononitroresorcinate (LMNR)	Priming compositions, electric detonators

* More common in FUDS-era munitions

Sampling Strategy

- For ranges, sampling and analysis based on release of primary explosives is not recommended
- Rationale:
  - Very small amount of primary explosive in any single munition
  - Sensitivity of primary explosives
  - Consumed if any part of the explosive train functions

Secondary Explosives

What are Secondary Explosives?

- Secondary explosives are relatively insensitive
- Used in booster and bursting charge (bulk of explosive charge)

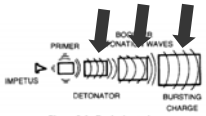
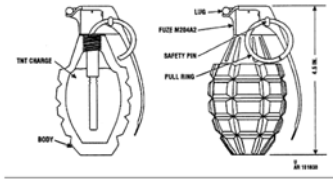


Figure 3-1. Explosive train.

Source: TM 9-1300-214 Military Explosives, Sep-1984

Example: Secondary Explosives



Tabulated Data:

Grenade (with fuze):
- Model(s): MK2
- Body: Cast iron
- Weight: .21 oz
- Length (max): 4.5 in.
- Diameter: 2.25 in.
- Color: Olive drab, or olive drab w/yellow band around top of fuze well

Explosive Filler:
- Type: TNT (flaked or granular)
- Weight: .2 oz

Fuze:
- Model(s): M204A1, M204A2
- Type: Pyro delay-detonating
- Primer: M42
- Detonator: Lead azide, lead styphnate, and RDX

MK2 fragmentation hand grenade

Source: TM 43-0001-29 Army Ammunition Data Sheets For Grenades

MK2 Grenade PEP Report

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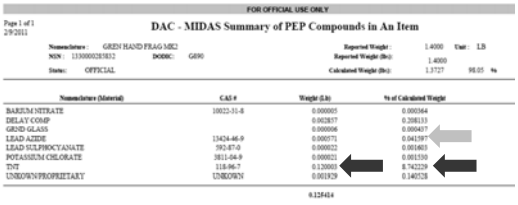
DAC - MIDAS PEP Structure in An Item

Nomenclature : GREN HAND FRAG MK2 — Reported Weight: 1.4000 Unit : LB
NSN : 1330000285832 DODIC: G890 — Reported Weight (lbs): 1.4000
Status: OFFICIAL — Calculated Weight (lbs): 1.3727 98.05 %

Drawing #	Std./Alt.	Nomenclature (Material)	Type	Reported Weight	Unit	Calculated Factor	Factored Weight (Lb)	Specification	TSCS
82-0-41B	STD	CHG	P	0.1200	LB	1	0.120000	MIL-T-248	
	STD	TNT	Mtl					MIL-T-248	
	STD	TNT (118-96-7) (100%)	Cmpd					MIL-T-248	
74-2-27B	STD	CHG PRIMER	P	0.4000	GR	1	0.000057	74-2-27	
	STD	PRIMER MIX MK3	Mtl					74-2-27	
	STD	LEAD SULPHOCYANATE (592-87-0) (38.13%)	Cmpd					50-11-13	
	STD	POTASSIUM CHLORATE (3811-04-9) (37.05%)	Cmpd					50-11-11	/4A/2/
	STD	GRND GLASS (10.45%)	Cmpd					50-11-23	
	STD	BARIUM NITRATE (10022-31-8) (8.68%)	Cmpd					50-11-20	/4A/
	STD	TNT (118-96-7) (5.69%)	Cmpd					50-13-5	/4B/
	STD	DELAY COMP	P	20.0000	GR	1	0.002857	VENDOR ITEM	
	STD	DELAY COMP	Mtl					VENDOR ITEM	
	STD	DELAY COMP (100%)	Cmpd					VENDOR ITEM	
	STD	PETN	P	13.5000	GR	1	0.001929	FSS-890	
	STD	PETN	Mtl					FSS-890	
	STD	INTERMEDIATE CHG (LEAD AZIDE)	P	4.0000	GR	1	0.000571	MIL-L-3055	
	STD	LEAD AZIDE	Mtl					MIL-L-3055	/1///
	STD	LEAD AZIDE (13424-46-9) (100%)	Cmpd					MIL-L-3055	/1///

0.125414

MK2 Grenade PEP Summary



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DAC - MIDAS Summary of PEP Compounds in An Item

Nomenclature : GREN HAND FRAG MK2 — Reported Weight : 1.4000 Unit : LB
NSN : 1330000285832 DODIC: G890 — Reported Weight (lbs): 1.4000
Status: OFFICIAL — Calculated Weight (lbs): 1.3727 98.05 %

Nomenclature (Material)	CAS #	Weight (Lb)	% of Calculated Weight
BARIUM NITRATE	10022-31-8	0.000005	0.000364
DELAY COMP		0.002837	0.206133
GRND GLASS		0.000006	0.000437
LEAD AZIDE	13424-46-9	0.000571	0.041597
LEAD SULFOCYANATE	592-87-0	0.000022	0.001601
POTASSIUM CHLORATE	3811-04-9	0.000021	0.001530
TNT	118-96-7	0.120000	8.742229
UNKNOWN PROPRIETARY	UNKOWN	0.001929	0.140528
		0.125414	

United States Booster and Secondary Explosives

Aliphatic Nitrate Esters	
1,2,4-Butanetriol Trinitrate	BTN
Diethyleneglycol Dinitrate	DEGN
Nitrocellulose	NC
Nitroglycerin	NG
Nitrostarch	NS
Pentaerythritol Tetranitrate	PETN
Triethylene Glycoldinitrate	TEGN
1,1,1-Trimethylolethane Trinitrate	TMETN
Nitramines	
Octahydro 1,3,5,7 tetranitro 1,3,5,7 tetrazocine	HMX
Hexahydro 1,3,5 trinitro 1,3,5 triazine	RDX
Ethylenediamine Dinitrate	EDDN
Ethylenedinitramine	Haleite
Nitroguanidine	NQ
2,4,6-Trinitrophenylmethylnitramine	Tetryl
Nitroaromatics	
Ammonium Picrate	AP
1,3-Diamino-2,4,6-Trinitrobenzene	DATB
2,2',4,4',6,6'-Hexanitroazobenzene	HNAB
1,3,5-Triamino-2,4,6-Trinitrobenzene	TATB
2,4,6-Trinitrotoluene	TNT
Other	
Ammonium Nitrate	

Source: TM 9-1300-214 Military Explosives, Sep-1984

Explosive Compositions

Binary Mixtures

Amatols	ammonium nitrate and TNT
Composition A	RDX and a desensitizer
Composition B	RDX and TNT
Composition C	RDX and plasticizer
Composition CH6	RDX, calcium stearate, graphite, polyisobutylene
Ednatols	haleite (ethylene dinitramine) and TNT
Octols	HMX and TNT
Pentolite	PETN and TNT
Picratol	ammonium picrate and TNT
Tetrytols	TNT and Tetryl
Tritonal	TNT and flaked Al

Source: TM 9-1300-214 Military Explosives, Sep-1984

Ternary Mixtures

Amatex 20	RDX, TNT, ammonium nitrate
Ammonal	ammonium nitrate, powdered Al, TNT, DNT, or RDX
High Blast Explosives	RDX, TNT, Al
HTA-3	HMX, TNT, and aluminum mixture 3
Minol-2	TNT, ammonium nitrate, Al
Torpex	RDX, TNT, Al

Source: TM 9-1300-214 Military Explosives, Sep-1984

Quaternary Mixtures

Depth bomb explosive (DBX)	TNT, RDX, ammonium nitrate, Al

Source: TM 9-1300-214 Military Explosives, Sep-1984

Explosives are found in what part of the munition?

- Projectile (i.e. mortars, artillery)
- Warhead (rocket)
- Bomb
- Mine

Degradation Products

Degradation Products

- Organic compounds can be transformed (degraded) in the environment
- Abiotic transformation
  - ►Photolysis
- Biotic transformation
  - ►Aerobic
  - ►Anaerobic

Analytical Methods

Field Analytical Methods

- Expray - Plexus Scientific
- Explosives Detection Field Test Kit - DropEx Plus
- EPA 8510 - Colorimetric Screening Procedure for RDX and HMX in Soil
- EPA 8515 - Colorimetric Screening Method for Trinitrotoluene (TNT) in Soil
- EPA 4050 - TNT Explosives in Soil by Immunoassay
- EPA 4051 - Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in Soil by Immunoassay

Laboratory Analytical Methods

- EPA 8095 Explosives by Gas Chromatography
- EPA 8330 Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)
- EPA 8332 Nitroglycerine by High Performance Liquid Chromatography
- CHPPM Method GC; isoamyl acetate extraction
- LC/MS
  - Modified EPA 8321A Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection
- PETN modified EPA 8330
- NG modified EPA 8330

Fate & Transport

Physical Properties

Analyte	Molecular Weight	Melting Pt. (°C)	Boiling Pt. (°C)	Water Solubility (mg/L)	Log K_{ow}
TNT	227.13	80.1-81.6	240 (explodes)	130 @ 20°C	1.86
RDX	222.26	204.1	(decomposes)	42 @ 20°C	0.86
HMX	296.16	276-280	(decomposes)	5.0 @ 25°C	0.061
TNB	213.11	122.5	315	34 @ 20°C	1.18
DNB	168.11	89.6	300-303	460 @ 15°C	1.49
Tetryl	287.14	129.5	(decomposes)	80	1.65
2,4-DNT	182.15	70	300 (decomposes)	270 @ 22°C	1.98
2,6-DNT	182.15	64-66		206 @ 25°C	2.02
2-Am-4,6-DNT	197.17	176		2800	1.94
4-Am-2,6-DNT	197.17	171		2800	1.91
NG	227	13.2		1500 @ 20°C	2.0
AP	246	123		10,000	0.02
PETN	316	141.3		0.99	

Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

06: Propellants

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Environmental Monitoring & Data Quality Workshop
29 March 2011

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Propellants

- Single-base
- Double-base
- Triple-base
- Composite
- Black Powder

Source: TM 9-1300-214 Military Explosives, Sep-1984

Single-base Propellants

- Primarily nitrocellulose (NC)
- Stabilizer
- may contain inorganic nitrates, nitrocompounds, and nonexplosive materials

Compositions of Single-Base Powders for Small Arms

USACE Common Operations Reports, PEP Table 9

	IMR	I	II	III	IV
Nitrocellulose	97.4%	99.3%	98.3%	99.0%	98.95%
Tin	2.0	--	--	--	--
Potassium Sulfate	--	--	1	--	--
Diphenylamine	0.6	0.7	0.7	1.0	1.05
Graphite	Glaze	Glaze	Glaze	Glaze	Glaze
Dinitrotoluene	Coat	Coat	Coat	Coat	Coat

Double-base Propellants

- Nitrocellulose (NC) and nitroglycerin (NG)
- Stabilizer
- Other additives

Double-Base Cannon Propellants

USACE Common Operations Reports, PEP Table 10

	M2	M5	M26A1
Nitrocellulose	77.45%	81.95%	68.7%
Nitroglycerin	19.50	15.00	25
Barium Nitrate	1.40	1.40	
Potassium Nitrate	0.75	0.75	
Ethyl Centralite	0.60	0.60	6
Graphite	0.30	0.30	0.3

Triple-base Propellants

- Nitrocellulose (NC), nitroglycerin (NG), and nitroguanidine (NQ)
- Stabilizer
- Other additives

Standard Artillery Propellant Compositions

USACE Common Operations Reports, PEP Table 8

	M15	M30	M31
Nitrocellulose (12.6% Nitrogen)	--	28%	20%
Nitrocellulose (13.15% Nitrogen)	20.0%		
Nitrocellulose (13.25% Nitrogen)	--		
Nitroglycerin	19.0	22.5	19
Nitroguanidine	54.7	47.7	54.7
Cryolite	0.3	0.3	0.3
Diphenylamine	--		1.5
Ethyl Centralite	6.0	1.5	
Diethylphthalate			4.5

Composite Propellants

- Fuel (e.g. metallic aluminum)
- Binder (normally organic polymer, e.g. synthetic rubber)(also a fuel)
- Inorganic oxidizing agent (e.g. ammonium perchlorate)

Pershing Missile motor propellant

68%	Ammonium perchlorate
13.2%	Polybutadiene acrylic acid
16%	Aluminum
2.8%	ERL-2795 (a curing agent)

Black Powder

Black Powders Used in Pyrotechnics

Components (%)	146	147	148
Potassium nitrate	74.0	70	-
Sodium nitrate	-	-	72
Charcoal	15.6	-	16
Coal (semibituminous)	-	14	-
Sulfur	10.4	16	12

Propellants are found in what part of the munition?

- Cartridge case (small arms, medium caliber munitions, some artillery)
- External to the projectile (mortars, some artillery)
- Rocket motor
- Explosive charge in some munitions

Analytical Methods

Laboratory Analytical Methods

- Nitrocellulose (NC)
  - No good analytical method
  - Relatively non-toxic
- Nitroglycerin (NG)
  - EPA 8332 Nitroglycerine by High Performance Liquid Chromatography
  - LC/MS
    - Modified EPA 8321A Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection
  - modified EPA 8330
- Nitroguanidine (NQ)
  - No published analytical method

Laboratory Analytical Methods (2)

- Perchlorate
  - EPA 6850 Perchlorate in Water, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry (HPLC/ESI/MS/MS)
  - EPA 6860 Perchlorate in Water, Soils and Solid Wastes Using Ion Chromatography/Electrospray Ionization/Mass Spectrometry (IC/ESI/MS or IC/ESI/MS/MS)
  - EPA 331.0 Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry
  - EPA 332.0 Determination of Perchlorate in Drinking Water by Ion Chromatography With Suppressed Conductivity And Electrospray Ionization Mass Spectrometry
  - EPA 314.0 Determination of Perchlorate in Drinking Water Using Ion Chromatography
  - EPA 314.1 Determination of Perchlorate in Drinking Water Using Inline Column Concentration/Matrix Elimination Ion Chromatography with Suppressed Conductivity Detection
  - EPA 9058 Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection
- Black Powder
  - No need for analysis

Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

07: Metals

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Environmental Monitoring & Data Quality Workshop
29 March 2011

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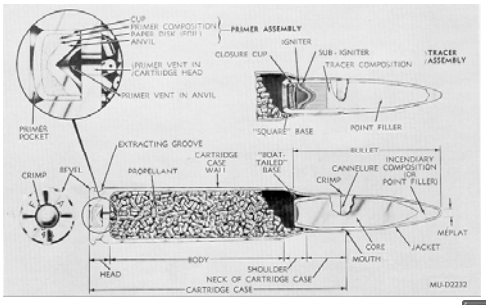
Source of Metals from Munitions

- Cartridge Case
- Projectile Case
- Bomb Case
- Filler (bursting charge, active component)

Small Arms Ammunition



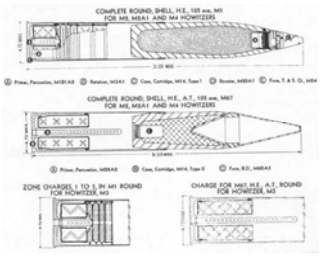
Metals in Small Arms Ammunition

- Cartridge Case
  - ► Brass – copper (70%) and zinc (30%)
- Bullet (projectile)
  - ► All military bullets are jacketed (clad) – FMJ (Full Metal Jacket)
    - Bullet jackets are typically gilding metal - copper (95%) and zinc (5%)
  - ► Bullet core composition depends upon caliber and type of ammunition

Bullet Cores

- .30 caliber
  - ► M2, Ball – lead (99%) and antimony (1%)
  - ► M2, AP – steel [iron (98%) and manganese (0.75%)]
- .50 caliber
  - ► M2, Ball – steel [iron (99%) and manganese (0.45%)]
  - ► M2, AP - steel [iron (98%) and manganese (0.75%)]

Artillery Ammunition



Shell, Semi-Fixed, 105-mm

Metals in Shell, Semi-Fixed, 105-mm, HEAT, M67

- Cartridge Case
  - Brass – copper (70%) and zinc (30%)
- Projectile
  - Case – steel [iron (98%) and manganese (1.5%)]
  - Rotating band – copper (90%) and zinc (9.9%)
  - Cone – copper (99%)
  - Ogive – steel [iron (99%) and manganese (0.45%)

Corrosion Products

Corrosion Products

- Metals corrode in the environment
- Generally form oxidized species
  - Thermodynamics
  - Kinetics

Analytical Methods

Field Analytical Methods

- EPA 6200 Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
  - XRF

Laboratory Analytical Methods

- EPA 6010 Inductively Coupled Plasma-Atomic Emission Spectrometry
- EPA 6020 Inductively Coupled Plasma-Mass Spectrometry
- EPA 7010 Graphite Furnace Atomic Absorption Spectrophotometry
- EPA 7470A Mercury in Liquid Waste (Manual Cold-Vapor Technique)
- EPA 7471B Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)

Fate & Transport

It's complicated!

Iron (Fe)

- Occurrence in munitions
  - Present as steel in cases and projectiles
- Regulatory status
  - Not a hazardous substance
- Common oxidation states
  - Fe(0); Fe(II); Fe(III)
- Crustal abundance
  - 6.3e+04 ppm (6.3%)
- RSLs (residential soil)
  - 5.5e+04 ppm

Lead (Pb)

- Occurrence in munitions
  - Present in small arms bullets and one practice bomb
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Pb(0), Pb(II)
- Crustal abundance
  - 14 ppm
- RSLs (residential soil)
  - 4e+02 ppm

Copper (Cu)

- Occurrence in munitions
  - Present in cartridge cases (brass) and bullet jackets (e.g. gilding metal)
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Cu(0), Cu(II)
- Crustal abundance
  - 50 ppm
- RSLs (residential soil)
  - 3.1e+03 ppm

Zinc (Zn)

- Occurrence in munitions
  - Present in cartridge cases (brass), bullet jackets (e.g. gilding metal), and one practice bomb
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Zn(0), Zn(II)
- Crustal abundance
  - 75 ppm
- RSLs (residential soil)
  - 2.3e+04 ppm

Aluminum (Al)

- Occurrence in munitions
  - Present in rocket cases, some propellants (powdered Al), and pyrotechnics (powdered Al)
- Regulatory status
  - Not a hazardous substance
- Common oxidation states
  - Al(0), Al(III)
- Crustal abundance
  - 8.2e+04 ppm (8.2%)
- RSLs (residential soil)
  - 7.7e+04 ppm

Manganese (Mn)

- Occurrence in munitions
  - Present in some steel alloys
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Mn(0), Mn(II), Mn(III)
- Crustal abundance
  - 950 ppm
- RSLs (residential soil)
  - 1.8E+03 ppm

Chromium

- Occurrence in munitions
  - Present in some steel alloys
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Cr(0), Cr(III), Cr(VI)
- Crustal abundance
  - 100 ppm
- RSLs (residential soil)
  - NA

Antimony (Sb)

- Occurrence in munitions
  - Present in alloys with lead in small arms bullets (99% Pb, 1% Sb)
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Sb(0), Sb(III), Sb(V)
- Crustal abundance
  - 0.2 ppm
- RSLs (residential soil)
  - 3.1e+01 ppm

Arsenic (As)

- Occurrence in munitions
  - Present in alloys with lead in shotgun pellets (96.4% Pb; 3% Sb; 0.6% As)
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - As(0), As(III); As(V)
- Crustal abundance
  - 1.5 ppm
- RSLs (residential soil)
  - 3.9e-01

Mercury (Hg)

- Occurrence in munitions
  - Present in some primer mixtures (mercury fulminate; used prior to WWII)
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - Hg(0); Hg(II)
- Crustal abundance
  - 0.05 ppm
- RSLs (residential soil)
  - 2.3e+01

Barium

- Occurrence in munitions
  - Present as barium nitrate in some pyrotechnics
- Regulatory status
  - Not a hazardous substance
- Common oxidation states
  - Ba(II)
- Crustal abundance
  - 500 ppm
- RSLs (residential soil)
  - 1.5e+04

Strontium

- Occurrence in munitions
  - Present in some pyrotechnics (e.g. tracer compositions)
- Regulatory status
  - Not a hazardous substance
- Common oxidation states
  - Sr(II)
- Crustal abundance
  - 370 ppm
- RSLs (residential soil)
  - 4.7E+04

Tungsten (W)

- Occurrence in munitions
  - Present in some armor penetrator rounds and some small arms bullets ("green bullets")
- Regulatory status
  - Not a hazardous substance
- Common oxidation states
  - W(0), W(VI)
- Crustal abundance
  - 160 ppm
- RSLs (residential soil)
  - NA

Uranium

- Occurrence in munitions
  - Some armor penetrators contain Depleted Uranium
- Regulatory status
  - Hazardous substance
- Common oxidation states
  - U(0), U(IV), U(VI)
- Crustal abundance
  - 1.8 ppm
- RSLs (residential soil)
  - 2.3e+02

Munitions Constituents (MC) and the Military Munitions Response Program (MMRP)

09: MC Considerations Related to MEC Operations

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29 March 2011

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Topics

- Consider the impact on MC sampling representativeness, spatial data, and overall waste disposal requirements based on choice of:
- MEC Removal Technology
  - ►Engineering Controls for Unintentional Detonations
- MEC Disposal Technology Options
  - ►Engineering Controls for Intentional Detonations

MEC Removal Technology Options

- Hand excavation
- Mechanically-Assisted Removal Using Excavating Equipment
- Remotely-Operated Equipment
- Armored Excavation and Transportation
- Mechanized Soil Processing (Screens/ Conveyors/Magnets)

Excavation

- Hand excavation
  - Industry standard, best access to soil for sampling and for visibility of potential MC sources
- Mechanically-Assisted Removal Using Excavating Equipment
  - Used in conjunction with hand excavation; no additional advantages

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Remote Operations and Armor

- Remotely-Operated Equipment
  - Limited to R&D at this time; selection of specific sample location/depth would be more difficult.
- Armored Excavation and Transportation
  - Focuses on mass excavation; potential MC sources lose spatial identity; selection of specific sample location/depth would be more difficult.

Armored Excavator

5 BUILDING STRONG®

Mechanized Soil Processing (Screens/ Conveyors/Magnets)

- Separates ordnance (or bullets being recovered for lead recycling) from soil
- Soil processed no longer has spatial identity – post processing sampling would be located based on piles generated during processing
- Soil is also somewhat mixed by process

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Engineering Controls – Unintentional Detonations

- Intrusive efforts frequently require engineering controls, which must be considered in sampling strategies
- Barricades limit access to soil that might be available to sample, but their use is required to protect nearby activities from unintentional detonations
- Spatial limitations may provide less bias than restricting samples to areas outside the exclusion zone (limiting samples to strictly those taken with anomaly avoidance)

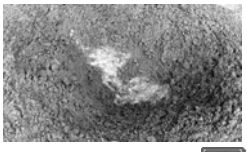
Open Front Barricades

MEC Disposal Technology Options

- Blow-in-Place
- Consolidated Shot
- Laser Initiation
- Contained Detonation Chamber
- Render Safe Procedures

Blow-in-Place

- Intact rounds that are detonated by blow-in-place typically leave less contamination than rounds that go low order, but greater contamination than if the round had functioned as designed (high order)
- Sampling related to BIPs may be impacted by engineering controls (see following slide)



Explosive Residues from Blow-in-Place Detonations of Artillery Munitions, Pennington, et al., Soil and Sediment Contamination: An International Journal,17:2,163 -180

ERDC/CRREL TR-06-13, Comparison of Explosives Residues from the Blow-in-Place Detonation of 155-mm High-Explosive Projectiles

Engineering Controls – Intentional Detonations

- Sand bags are common means of controlling intentional detonations (BIPs)
- If sand bags are required, consider the impacts on post detonation sampling – where is media representative of the site?

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BIP + Low Order?

- Likely MC source
- Low Orders documented MC source; BIP data from low orders can be particularly high
- Sample:
  - 5" Armor Piercing HE Low Order BIP
  - TNT – 1400 mg/kg
    - 19 mg/kg (res)
    - 79 mg/kg (ind)

More on Low Order MC Sources:
Explosive Residues from Low-Order Detonations of Heavy Artillery and Mortar Rounds, Pennington, et al; Soil and Sediment Contamination: An International Journal,17:5,533 - 546

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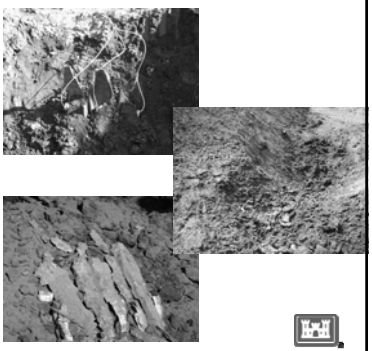
Consolidated Shots

- Multiple rounds are detonated together; must be "acceptable to move"
- MC results more analogous to OD area
- Sample result:
  - TNT – 43-53 mg/kg
    - 19 mg/kg (res)
    - 79 mg/kg (ind)



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Laser Initiation

- HNC conducted study during development of release of MC to soil and air
- Study showed that release was higher from initiation by laser than by C4 donor charge for low orders and for many high orders.
- Laser systems do not require donor charges; this is their primary advantage.
- Secondary waste stream issues and sampling needs are similar to BIPs

Contained Detonation Chambers

- CDCs are used to destroy MEC, while containing both the blast effects and the secondary waste stream within the closed system.
- Air handling and filtration may be required depending on the munitions being detonated.
- Secondary waste streams must be characterized and disposed of properly. They typically include:
  - Pea gravel
  - Torit filter dust
  - Decontamination water
- Use is limited to items that are within the net explosive weight (NEW) the system is approved to destroy and contain fill the unit is approved to destroy:
  - Conventional munitions, such as
    - Energetics
    - White phosphorus
    - Riot agent
    - Propellants
    - Smoke,
  - Approval does not include plasticized white phosphorus
  - Single site approval has been granted for chemical munitions

Contained Detonation Chambers (cont'd)

- Plan for cost and schedule impacts of manifesting and disposal
- Example Waste Profile Results:
  - Pea Gravel
    - D008 (Pb)
    - D006 (Cd)
    - D003 (Reactive) – WP munitions
  - Filters
    - D002 (Corrosive) – FS munitions
  - Decon water
    - Nonhazardous
    - Hazardous (lead)

Render Safe Procedures

- Military personnel only, high hazard to personnel performing procedure
- If circumstances were such that it were approved, sampling would only be permitted after munition was removed
- No MC release unless casing was compromised due to corrosion or previous sympathetic detonation.

Questions?

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